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<p>(21) International Application Number: PCT/US92/08240 (22) International Filing Date: 28 September 1992 (28.09.92)  (30) Priority data: 765,884 26 September 1991 (26.09.91) US  (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: MAHLER, Walter ; 913 Barley Drive, Box 4006, Wilmington, DE 19807 (US). (74) Agents: SHIPLEY, James, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Record Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: COMPOSITIONS AND PROCESS FOR USE IN REFRIGERATION</p> <p>(57) Abstract</p> <p>A blend of (a) at least 10 % of 1,1,2,2-tetrafluoroethane with at least 10 % of one of 1,1,1,2-tetrafluoroethane and pentafluoroethane as refrigerant mixed with (b) a mono- or di-functional polyalkylene glycol based on 25-75 % propylene oxide and 75-25 % ethylene oxide having an SUS viscosity at 100 °F of 100 to 1200, is disclosed for use in compression refrigeration.</p>		

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TITLECompositions and Process for  
Use in Refrigeration

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Field of Invention

This invention relates to lubricants used with refrigerants in compression refrigeration and air-conditioning systems. More particularly, it relates to lubricants for use with saturated hydrocarbons having 1-4 carbon atoms that are partially or fully substituted with at least one atom of chlorine or fluorine, and have a normal boiling point of  $-80^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ . Specifically, this invention relates to lubricants for use with tetrafluoroethanes, e.g. 1,1,1,2-tetrafluoroethane (HFC-134a), and 1,1,2,2-Tetrafluoroethane (HFC-134). These compounds are being considered as replacements for dichlorodifluoromethane (CFC-12), particularly in automotive air conditioning systems.

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Background of Invention

Refrigeration systems that use CFC-12 as the refrigerant generally use mineral oils to lubricate the compressor. (See for example the discussion in Chapter 32 of the 1980 ASHRAE Systems Handbook). CFC-12 is completely miscible with such oils throughout the entire range of refrigeration system temperatures, i.e.  $-45^{\circ}\text{C}$  to  $65^{\circ}\text{C}$ . In automotive air-conditioning, paraffinic and naphthenic oils of about 500 SUS viscosity at  $100^{\circ}\text{F}$  are usually used with CFC-12. These oils have "pour points" below  $-20^{\circ}\text{C}$  and viscosities of about 55 SUS at  $210^{\circ}\text{F}$  and are completely miscible with the CFC-12 refrigerant over the range of temperatures from  $-10^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . Consequently, oil which dissolves in the refrigerant travels through the refrigeration loop in the air conditioning system and returns with

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the refrigerant to the compressor. It does not separate during condensation, although it may accumulate when the refrigerant is evaporated. At the same time, this oil which lubricates the compressor will contain some refrigerant which, in turn, may affect its lubricating properties.

When substituting HFC-134a or HFC-134 for CFC-12 in these refrigeration systems, it would be desirable to be able to use the same oils as used with CFC-12. It would not require any substantial change in equipment nor any significant changes in conditions used for the system. If lubricant separates from refrigerant during operation of the system, serious problems may result, i.e. the compressor could be inadequately lubricated. This would be most serious in automotive air-conditioning systems because the compressors are not separately lubricated and a mixture of refrigerant and lubricant circulates throughout the entire system. Unfortunately, however, the mineral oils are substantially immiscible with the tetrafluoroethanes.

Two publications of ASHRAE discuss the problems associated with separation of lubricants and refrigerants. These are "Fundamentals of Lubrication in Refrigerating Systems and Heat Pumps" Kruse and Schroeder ASHRAE Transactions Vol. 90, Part 2B, pps. 763-782, 1984 and "Evaluation of Lubricants for Refrigeration and Air-Conditioning Compressors", Spauschus, ibid pps. 784-798.

In summary, refrigerants which are not completely miscible with an oil in the full range of mixture compositions and operating temperatures may become miscible or immiscible as the temperature is raised or lowered from room temperature. The areas of immiscibility may assume a variety of shapes, i.e. parabolic or non-parabolic. As a parabola, the curve

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of miscibility temperature vs. percent oil in the mixture, may have its open or concave portion facing the low or high temperatures. The closed or convex portion of the parabolic curve identifies, respectively, the maximum or minimum temperature above or below which the refrigerant and the lubricating oil are completely miscible. These temperatures are referred to as the maximum or minimum "consolute temperatures." Beside parabolas, these curves can assume skewed parabolic shapes or curves of varying slope wherein immiscibility occurs above or below the curve.

One of the objects of this invention is to provide a combination of lubricating oil and tetrafluoroethane, e.g. HFC-134a and HFC-134, where the area of miscibility encompasses the full range of temperature and composition encountered in compression refrigeration, i.e. complete miscibility occurs for all compositions in the range of -10°C to at least 20°C, preferably from -45°C to at least 50°C. Another object is to provide a process for using such compositions in compression refrigeration.

#### Prior Art

U.S. Patent No. 4,248,726, issued February 5, 1981, and U.S. Patent No. 4,278,064, issued May 12, 1981, both to Nippon Oil Company et al, relate to the use of a polyglycol oil such as polyoxypropylene glycol (or an alkyl ether thereof) having a viscosity index of at least 150 and a glycidyl ether type epoxy compound as a high viscosity refrigeration oil composition for halogen-containing refrigerants. These polyglycol/-glycidyl ether compositions are disclosed for use with Freon®11, 12, 13, 22, 113, 114, 500 and 502; and as being "particularly effective" with Freon®12 or 22.

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Research Disclosure 17463 entitled

"Refrigeration Oil by E. I. du Pont de Nemours and Company discloses polyalkylene glycols such as Ucon® LB-165 and Ucon® LB-525 sold by Union Carbide Corporation, for use with HFC-134a. These glycols are polyoxypropylene glycols that are mono-functional and are prepared from propylene oxide initiated with n-butanol. The publication states that these combinations of oil and refrigerant are miscible in all proportions at temperature at least as low as -50°C and are thermally stable in the presence of steel, copper and aluminum at 175°C for about six days. However, as stated in U.S. Patent No. 4,755,316, Col. 5, line 14 ff. the "Ucon" LB-525" has been found to be immiscible at above about +5°C with HFC-134a... Practically this means that such lubricants are not miscible with HFC-134a over most of the temperature range used in automotive air conditioning. For such use the miscible range should be from -40°C to at least +50°C or higher, above 90°C, if possible".

U.S. Patent No. 4,755,316, issued July 5, 1988, to Allied-Signal Inc. also relates to the use of polyalkylene glycols of the polyoxypropylene glycol type. These glycols are at least difunctional with respect to hydroxyl groups and contain at least 80% propylene units relative to the total, the remaining 20% may derive from ethylene or butylene oxide or esters, olefins and the like which are polymerizable with propylene oxide. It should be noted that only 100% oxypropylene units in the difunctional PAGs are exemplified in this patent and similarly, only 100% oxypropylene units in the monofunctional PAGs were disclosed in the Research Disclosure 17486; and, further, all the examples in this Allied-Signal patent involve HFC-134a. No examples involving HFC-134 are disclosed. It should also be noted from Table A in

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column 6 of this patent that several of the difunctional polyoxypropylene glycols claimed to be useful in this patent are not miscible with HFC-134a to at least 50°C, e.g. NIAX-1025 at 50 wt. % HFC-134a "to over 40°C", PPG-2000 at 85 wt % HFC-134a "to 13°C"; and PPG-2000 at 50 wt. % HFC-134a "to 43°C". It has also been found that the mixture of NIAX-425 at 30 wt. % HFC-134a is miscible to only -5°C, a far cry from -40°C, an absolute necessity for automotive air conditioning.

#### Summary of the Invention

The present invention is based on the discovery that the use of at least about 10% by volume of HFC-134, preferably at least 20%, most preferably at least 50%, in a blend with HFC-134a or HFC-125 will expand the miscibility range of the latter tetrafluoroethane, HFC-134a, or pentafluoroethane, HFC-125, with both the monofunctional and the difunctional polyalkylene glycols of the polyoxyethylene-polyoxypropylene type. Polyalkylene glycols of this type are defined as glycols that are either monofunctional or at least difunctional with respect to hydroxyl groups and contain 25-75% ethylene oxide units and 75-25% propylene oxide units. Other mils may derive from butylene oxide or hydroxylated esters, hydroxylated olefins and the like which are polymerizable with ethylene oxide and/or propylene oxide.

Thus, I have found that the use of a sufficient amount to lubricate, usually 10-20% by volume for automotive use, and in some situations as high as 50% by volume of at least one mono- or di-functional, preferably a random, polyalkylene glycol (PAG), also referred to as polyoxyalkylene glycol, based on a significant amount of ethylene oxide, in a

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random copolymer, preferably at least 25% ethylene oxide, and most preferably, 50% ethylene oxide and 50% propylene, will be completely miscible with a refrigerant blend of the tetrafluoroethanes, usually 80-90% by volume of the tetrafluoroethanes, the blend containing at least about 10% by volume of HFC-134 with the remainder of HFC-134a. This blend may also be blended with other refrigerants operating in the range of temperatures from -40°C to at least 50°C. It should also be understood that 100% HFC-134 is miscible with the aforementioned glycols of the 50-50 polyoxy-ethylene-polyoxypropylene type.

Basically, the use of 10% by volume of HFC-134 in a blend with 90% by volume of HFC-134a will expand the miscibility range of HFC-134a with the polyoxy-alkylene glycol (based on at least 25% ethylene oxide) by 20°C, i.e. +10°C at the upper end of the range and -10°C at the lower end. Surprisingly, in the compression cycles with 50 HB660 ( a mono functional polyoxyethylene-polyoxypropylene glycol having an SUS viscosity of 660 and prepared using butanol as initiator), the use of 20% by volume of 134 with the remainder being 134a will expand the miscibility range from -50°C to +31°C for HFC-134a alone to from -100°C to +54°C; and the use of 50% by volume of HFC-134 with HFC-134a will expand the miscibility range to -90°C to +72°C! Thus, although 10% by volume of HFC-134 with HFC-134a provides significant improvement, at least 20% is preferred and at least 50% HFC-134 is most preferred.

The weight ratio of refrigerant (HFC-134 or HFC-134 blended with HFC-134a) to the PAG lubricant in the mixtures used for refrigeration may be anywhere from 99/1 to 1/99, preferably 99/1 to 70/30. The viscosities of the polyalkylene glycols may be anywhere



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from 50 to 3000 SUS at 100°F but for most commercial uses, from 100 to 1200 SUS at about 100°F.

The process of manufacturing the mono-functional PAGs may involve initiation with methanol, ethanol, propanol or butanol. The last mentioned, butanol, is the preferred initiator; and the process of manufacture is described in the Encyclopedia of Polymer Science and Engineering, Volume 6, pps. 225-273; "Ethylene Oxide Polymers and Copolymers" by Clinton and Matlock, 2nd edition, 1986, John Wiley & Sons.

The process of manufacturing the di-functional PAGs may involve initiation with a glycol having anywhere from two to six carbon atoms between -OH groups. Diethylene glycol is the preferred initiator; and the process of manufacture is Engineering, Volume 6; "Ethylene Oxide Polymers and Copolymers" by Clinton and Matlock, 2nd edition, 1986, John Wiley & Sons.

It has been known that the use of an appropriate amount of an "extreme pressure additive" improves the lubricity and load-bearing characteristics of the butanol-initiated monofunctional random polyalkylene glycol having 50% oxyethylene units as set forth in the U.S. Application Serial No. 360,981 filed June 2, 1989; and it is known that the EP additives will also improve the quality of the refrigerant-lubricant compositions of this invention. EP additives for use in this invention are included among those disclosed in Table D of U.S. Patent 4,755,316. The preferred ones are the organic phosphates and include Lubrizol®1097, a zinc (dialkyl dithio) phosphate manufactured by the Lubrizol Corporation; and SYN-O-AD® 8478, a 70%/30% blend of tri (2,4, 6-tri-t-butyl phenyl) phosphate/-triphenyl

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phosphate manufactured by the Stauffer Chemical Company.

EP additives may also be used in conjunction with some of the anti-wear additives, oxidation and thermal stability improvers, corrosion inhibitors, viscosity index improvers, detergents and anti-foaming agents disclosed in Table D of U.S. Patent 4,755,316. These additives may also be partially or fully fluorinated. A preferred blend of additives is MLX-788, a proprietary mixture of Union Carbide Corporation containing a phosphate and two amine-containing compounds.

#### Description of Preferred Embodiments

As stated previously, HFC-134 and the blends of tetrafluoroethanes HFC-134a and HFC-134 have physical characteristics which allow substitution for CFC-12 with only a minimum of equipment changes in compression refrigeration. These blends could be further blended with other refrigerants, including CFC-12( $\text{CCl}_2\text{F}_2$ ), HCFC-22( $\text{CHClF}_2$ ), HFC-152a( $\text{CH}_3\text{CHF}_2$ ), HCFC-124( $\text{CHClFCF}_3$ ), HCFC-124a( $\text{CHF}_2\text{CClF}_2$ ), HFC-125( $\text{CHF}_2\text{CF}_3$ ), HCFC-142b( $\text{CH}_3\text{CClF}_2$ ), HFC-32( $\text{CH}_2\text{F}_2$ ), HFC-143a( $\text{CH}_3\text{CF}_3$ ), HFC-143( $\text{CHF}_2\text{CH}_2\text{F}$ ), and FC-218( $\text{CF}_3\text{CF}_2\text{CF}_3$ ); and for purposes of the present invention these latter blends are not excluded. However, only those blends of the tetrafluoroethanes with other refrigerants which are miscible with the lubricants of this invention in the range of  $-45^\circ\text{C}$  to about  $+20^\circ\text{C}$  are included.

HFC-134a may be prepared by any of the methods disclosed in the prior art; e.g., U.S. 2,745,886; 2,887,427; 4,129,603; 4,158,675; 4,311,863; 4,792,643 and British 1,578,933 and 2,030,981.

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HFC-134 may be prepared by the method disclosed by Wilford, Forster and Stone in Journal of The Chemical Society, 1965, 6519-6523.

5 The most preferred mono-hydroxyl polyalkylene glycol for use in this invention is based on the random polymerization of propylene oxide and ethylene oxide initiated with butanol. Although the viscosity can range from about 100 to 1200 SUS viscosity at 100°F, preferably 400 to 1200 SUS, the most preferred PAG is  
10 the "Ucon" 50 HB500, 500 representing the SUS viscosity at 100°F and "H" representing "hydrophylic", that is manufactured by the Union Carbide Corporation. The process for its manufacture is described in the 1986 edition of the Encyclopedia of Polymer Science and  
15 engineering.

The preferred 50HB500 oil has a pour point below -40°C, is completely miscible with the 10% blend of HFC-134 with HFC-134a from -50°C to condenser temperatures above 50°C, and meets all the other  
20 requirements for automotive air conditioning, i.e. viscosity index, stability, lubricity, and miscibility with the blend of HFC-134 and HFC-134a down to below -20°C. Furthermore, the use of an extreme pressure oil additive such as those mentioned previously should  
25 improve the load-carrying capability significantly.

Specifically, the lubricants used in the compositions of this invention, and in the invented method for providing lubrication in compression refrigeration and air-conditioning equipment have the  
30 following characteristics:

Viscosity at 100°F

50 to 3000 SUS, preferably 100 to 1200 SUS, particularly about 500 SUS for automotive  
35 air-conditioning

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Viscosity Index

Greater than 10, preferably at least 70 and higher

Pour Point

5        -10°C, preferably -10°C to about -45°C and  
         -20°C for the 100 SUS and 500 SUS oils,  
         respectively

Solubility or miscibility range

10       100% from 100°C to (a) less than -40°C to  
         about 20°C for 1-99 weight percent of the  
         blend of HFC-134 and HFC-134a in mixture with  
         the lubricant of 100°F viscosities of 50 SUS  
         to 3000 SUS (b) less than -10°C for the  
         preferred 500 SUS mixtures.

15       Four-ball wear test with a specific set of  
         steel balls. Scar wear and coefficient of  
         friction equal to or slightly higher than that  
         for the oils currently used with CFC-12 in  
         automotive air-conditioning, i.e., 0.37 mm  
20       scar wear and 0.07 friction coefficient when  
         saturated with CFC-12 at atmospheric pressure.

"Falex" (load failure) test with a specific  
         type of steel for the V-block and pin. The  
         fail load equal to or greater than that for  
25       the CC/refrigerant oil combinations, i.e.,  
         1300 lbs. when saturated with CFC-12 at  
         atmospheric pressure.

1. Solubility of Refrigerant in Lubricants

30       Six ml. blends of refrigerant (HFC134/134a)  
         and lubricant were used for the solubility studies.  
         Generally, the mixtures contained 30, 60, and 90 wt. %  
         refrigerant. These air-free mixtures were contained in  
         sealed Pyrex® tubes (7/16" I.D. x 5.5", ca. 12.5 cc  
35       capacity) or, as in Example 1 for the LB525 oil (1/8"

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I.D. x 5 7/8" length) where the liquid refrigerant and oil mixture occupied about 60 volume per cent of the tube at 25°C. Generally, a mixture containing about 83% by weight refrigerant and about 17% by weight oil was tested in these tubes. The refrigerant/lubricant solubilities were determined by completely immersing the tube in a bath at each test temperature for a minimum of 15 minutes and providing agitation to facilitate mixing and equilibration. The accuracy of determining the temperatures when the refrigerant/lubricant blend became either miscible or immiscible was about  $\pm 2^\circ\text{C}$ . The refrigerant/lubricant blends were called immiscible when the blend acquired and retained "schlieren" lines; or formed floc; or became cloudy; or formed two liquid layers. These solubility tests were run from about 93°C to at least -50°C. Tests were not run above 93°C for safety and practical reasons.

## 2. Viscosity and Viscosity Index

a. Viscosity is a property that defines a fluid's resistance to shearing force. It is expressed in terms of absolute viscosity, kinematic viscosity or Saybolt Universal Seconds viscosity (SUS), depending on the method by which it is determined. Conversion from SUS to  $\text{mm}^2/\text{s}$  (centistokes) can be readily made from tables contained in ASTM D-445, but it is necessary to know the density to convert kinematic viscosity to absolute viscosity. Refrigeration oils are sold in viscosity grades, and ASTM has proposed a system of standardized viscosity grades from industry-wide usage (D-2422).

b. Viscosity Index is a measure of the amount of change experienced by an oil with changes in temperature.

Viscosity decreases as the temperature increases; and increases as the temperature decreases.

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The relationship between temperature and kinematic viscosity is represented by:

$$\log \log (v + 0.7) = A + B \log T$$

where  $v$  = kinematic viscosity,  $\text{mm}^2/\text{s}$  (CST)

$T$  = thermodynamic temperature (kelvin)

$A, B$  = constants for each oil

This relationship is the basis for the viscosity temperature charts published by ASTM and permits a straight line plot of viscosity over a wide temperature range. This plot is applicable over the temperature range in which the oils are homogeneous liquids.

The slope of the viscosity-temperatures lines is different for different oils. The viscosity-temperature relationship of an oil is described by an empirical number called "the viscosity index" (VI) as referred to in ASTM D-2270. An oil with a high viscosity index (HVI) shows less change in viscosity over a given temperature range than an oil with a low viscosity index (LVI).

### 3. Pour Point

Any oil intended for low temperature service should be able to flow at the lowest temperature likely to be encountered. The procedure for determining pour point is described in ASTM D-97.

The invention will be more clearly understood by referring to the following experiments which are presented in Tables I - II.

Table I summarizes the solubility data for various blends of HFC-134 and HFC-134a as refrigerant with 20 volume per cent 50HB660, a monofunctional polyoxyalkylene glycol, as the lubricant. It will be noted that as little as 20% HFC-134 expands the solubility range from  $-50^\circ\text{C}$  to  $31^\circ\text{C}$  to a range of  $-100^\circ\text{C}$  to  $54^\circ\text{C}$ .

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Table II summarizes the solubility data for various blends of HFC-134 and HFC-134a (compared to 100% HFC-134a) as the refrigerant with 20 volume percent 50HB500, a monofunctional polyoxyalkylene glycol, as the lubricant.

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Both 50HB660 and 50HB500 are monofunctional polyoxyalkylene glycols prepared from 50 weight per cent ethylene oxide and 50 weight per cent propylene oxide using butanol as the end capping agent. The "660" glycol has an SUS viscosity at 100°F of 660; and the 10 "500" glycol, an SUS viscosity of 500.

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It will be noted that in all the experiments, refrigerant amounting to about 80% by volume of a blend of HFC-134 and HFC-134a together with 20% by volume of lubricant were used for the solubility studies. This 15 refrigerant-lubricant composition corresponds to the ratio generally employed in air-conditioning engines and is usually the least soluble mixture. These air-free mixtures were contained in sealed "Pyrex" glass tubes of 3mm inside diameter and 15 cm length. Compatibility was 20 determined by cooling or heating the tubes while fully immersed and observing phase separation which was signalled by the optically clear mixture turning cloudy.

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Table I

Solubility of Refrigerant  
(Blends of HFC-134/HFC-134a) in mixtures  
(80 volume % refrigerant/20 volume % lubricant)  
with 50HB500 as the lubricant

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Expt. No.	Vol. % HFC-134 in the HFC 134/ HFC 134a blend	Miscible Range (°C)
10	1	93* to -78*
	2	89 to -60*
	3	75 to -60*
	4	55 to -60*
15	5	40 to -60*

\*Test was discontinued; miscibility would probably  
extend beyond these temperatures.

20

Table II

Solubility of Refrigerant  
(Blends of HFC-134/HFC-134a) in mixtures  
(80 volume% refrigerant/20 volume % lubricant)  
with 50HB660 as the lubricant

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Expt. No.	Vol.% HFC-134 in HFC 134/ HFC 134a blend	Miscible Range (°C)
30	6	93* to - 78*
	7	85* to -100*
	8	70 to -100*
	9	54 to -100*
35	10	31 to - 50*



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\*Test was discontinued; miscibility would probably extend beyond these temperatures.

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CLAIMS

What is claimed is:

1. A composition for use in compression refrigeration comprising:
  - (a) a refrigerant containing at least 10% by volume of 1,1,2,2-tetrafluoroethane in a blend with at least 10% by volume of at least one of 1,1,1,2-tetrafluoroethane and pentafluoroethane; and
  - (b) a lubricant comprising at least one monofunctional polyalkylene glycol with respect to hydroxyl groups, based on 25-75% ethylene oxide units and 75-25% propylene oxide units, having an SUS viscosity at 100°F of 100 to 1200 and being miscible in combination with said refrigerant in the range of temperatures from -40°C to at least +20°C.
2. The composition of Claim 1 wherein said refrigerant comprises at least 20% by volume of 1,1,2,2-tetrafluoroethane in a blend with at least 20% by volume of 1,1,1,2-tetrafluoroethane.
3. The composition of Claim 1 wherein said mono-functional polyalkylene glycol has an SUS viscosity at 100°F of 500.
4. The composition of Claim 1 wherein said mono-functional polyalkylene glycol is based on 50% propylene oxide units and 50% ethylene oxide units.
5. A method for improving lubrication in compression refrigeration equipment using a refrigerant containing at least 10% by volume of 1,1,2,2-tetrafluoroethane in a blend with at least 10% by volume of at least one of 1,1,1,2-tetrafluoroethane and

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pentafluoroethane and using 1-99% by weight of a lubricant comprising at least one mono-functional polyalkylene glycol with respect to hydroxyl groups, based on 25-75% ethylene oxide units and 75-25% propylene oxide units, in combination with said refrigerant, said lubricant having an SUS viscosity of 100-1200 at 100°F.

6. A composition for use in compression refrigeration comprising:

(a) a refrigerant comprising at least 20% by volume of 1,1,2,2-tetrafluoroethane in a blend with at least 20% by volume of at least one of 1,1,1,2-tetrafluoroethane and pentafluoroethane; and

(b) a lubricant comprising at least one polyalkylene glycol which is di-functional with respect to hydroxyl groups, based on 25-75% ethylene oxide units and 75-25% propylene oxide units, having as SUS viscosity at 100°F of 100 to 1200 and being miscible in combination with said refrigerant in the range of temperatures from -40°C to at least +20°C.

7. The composition of Claim 6 wherein said refrigerant comprises about 20% by volume of 1,1,2,2-tetrafluoroethane in a blend with about 80% by volume of 1,1,1,2-tetrafluoroethane.

8. The composition of Claim 6 wherein said refrigerant comprises about 50% by volume of 1,1,2,2-tetrafluoroethane in a blend with about 50% by volume of 1,1,1,2-tetrafluoroethane.

9. The composition of Claim 6 wherein the SUS viscosity at 100°F of said polyalkylene glycol is from 400 to 1000.

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10. A method for improving lubrication in  
compression refrigeration equipment using a refrigerant  
comprising at least 20% by volume of 1,1,2,2-tetra-  
fluoroethane in a blend with at least 20% by volume of  
5 at least one of 1,1,1,2-tetrafluoroethane and penta-  
fluoroethane and using 1-99% by weight of a lubricant  
comprising at least one polyalkylene glycol which is  
difunctional with respect to hydroxyl groups, based on  
25-75% ethylene oxide units and 75-25% propylene oxide  
10 units in combination with said refrigerant, said  
lubricant having an SUS viscosity of 100-1200 at 100°F.

11. The method of Claim 10 wherein said  
lubricant is based on 50% propylene oxide units and 50%  
15 ethylene oxide units.

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## INTERNATIONAL SEARCH REPORT

International Application

PCT/US 92/08240

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C10M107/34; C10M171/00; C09K5/04; //(C10N20:02) (C10N40:30)		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C10M ; C09K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	WO,A,9 109 090 (E.I DU PONT DE NEMOURS AND COMPANY) 27 June 1991 see page 5, line 9 - line 17 see page 6, line 10 - line 33 ---	1-11
Y	EP,A,0 402 009 (E.I DU PONT DE NEMOURS AND COMPANY) 12 December 1990 see page 3, line 19 - line 31 see page 3, line 52 - line 55 see page 8; table II ---	1-11
A	EP,A,0 400 894 (E.I DU PONT DE NEMOURS AND COMPANY) 5 December 1990 see page 3, line 19 - line 30 -----	1,4-6, 9-11
<p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
02 DECEMBER 1992	23. 12. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	HILGENGA K.J.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9208240  
SA 65537**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 02/12/92

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